LASER-INDUCED INTERACTION OF SILICA WITH METHANE

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INTRODUCTION

Laser distillation technique advanced by investigations of energy balance in a laser plume formed on the surface of silica (SiO_2) under the action of radiation of the 10.6 mm wavelength was proposed in [1]. The small depth of absorption (≤20 μm) and the low thermal conductivity resulted in surface heating of silica glass, accompanied by sublimation at $T_s > 1.8$ kK. A continuous laser plume appeared at the laser radiation intensities 1 - 6 kW/cm^2 when the target surface was heated to a temperature exceeding the boiling point $T_b \approx 3$ kK [2,3] and the saturated vapor pressure above the surface rose above the atmospheric value. At this laser radiation power the rate of loss of the target material by sublimation of ~3 mg/s and the specific laser radiation energy of evaporation of silica glass was of 30 kJ/g. A continuous laser plume at the tip of a silica glass rod in air represented a gasdynamic jet of the products of sublimation of SiO_2 at temperatures $T \geq T_b$ escaping into the surrounding atmosphere. According to thermo-chemical analyses [3] at the boiling point T_b thermal decomposition of SiO_2 occurs and composition of the saturated vapor above SiO_2 is governed by equilibrium chemical reaction $SiO_2 \rightarrow 57.6\ SiO + 6.6\ O + 25.8\ O_2 + 10.0\ SiO_2$. Cooling of the gaseous products of sublimation by the emission of thermal radiation and by heat exchange with the ambient gas resulted in chemical recombination of these products and condensation of SiO_2 in submicron particles. Deposition of particles on substrates during continuous laser distillation of SiO_2 resulted in synthesis of bulk samples of porous and vitreous structure varied with the temperature of substrates. Laser distillation is useful for rapid synthesis of high-purity and doped samples of silica materials with variable optical properties, including silica nanocomposites [4]. Fluorine-doped silica glasses were synthesized by initiating chemical reactions of the products of pyrolysis in a laser plume with a gas containing freon [5].

Chemical reduction of silica SiO_2 with carbon, hydrogen, and hydrocarbons occurs at high temperatures [6]. Initial stage of the synthesis of Si crystals is smelting of metallurgical silicon in electric furnaces at temperatures 2 - 6 kK in reactions of reduction of natural silica's with carbon [7]. We investigated experimentally physicochemical processes induced by laser plume on silica glass laser targets streamlined by CH_4 - Ar gas flows, composition and microstructure of products of SiO_2 reduction reactions deposited on substrates [8].

EXPERIMENTAL

Experiments were made with laser targets in the form of cylindrical rods of high-purity and technical-grade silica glass of diameters $d \approx 3$ mm. Experimental setup is shown in Fig.1. A diverging beam from a cw electric-discharge CO_2-laser of ~80 W power was directed on the tip of the rods located behind the focus of an NaCl lens (F = 27 cm) to enhance the stability of the configuration of the resultant laser plume. The radiation intensity was varied by altering the distance from the focus to the target. The targets were placed inside a silica tube of 25 cm length and inner diameter of 15 mm and streamlined by gas flow directed along the tube opposite to the laser beam and escaped freely into atmosphere. A neutral gas flow surrounding the laser target was provided with Ar, whereas reducing flow consisted of CH_4 or of a CH_4 - Ar mixture. The gas flow rate at atmospheric pressure did not exceed 1 liter/min. Silica rods and tubes were used as substrates for the deposition of the laser plume products. The chemical composition of the powder layers deposited on the substrates, sintered or compacted into pellets, was measured with a Camebax SX50 x-ray microanalyser. Microstructure of the laser targets and of the deposited materials was investigated with optical and electron microscopes.

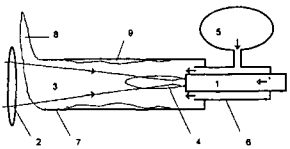

Figure 1. Experimental setup: (1) laser target, (2) NaCl lens, (3) laser beam, (4) laser plume, (5) CH_4 - Ar gaseous mixture, (6) support of the laser target , (7) silica glass tube substrate, (8) flame at the edge of the silica tube, (9) products of the reactions.

RESULTS

At a fixed laser radiation intensity the length of the plume and the spectrum of the emitted radiation depended on the target material. The luminous part of the plume was of ~5 mm length and the emission spectrum was continuous in the visible range when the plume was formed on the surface of high-purity silica glass in an air atmosphere and in Ar. Emission spectra of the plume formed on technical-grade silica glasses included resonance lines of Na and/or K, and the length of the plume increased to ~10 mm. The partly melted and solidified tips of high purity silica glass rods subjected to laser irradiation in atmosphere and Ar had an optically smooth convex shape when the diameter of the laser spot on the end was $d_l > 1/3d$ and a concave shape when d_l was less. Approaching to the focus resulted in a crater formation of ~1 cm deep. The stability of the configuration of targets subjected to laser irradiation was evidently governed by high viscosity of silica glass even at temperature ~T_b.

Radically different results were obtained at the same irradiation geometry when the gas flow around the laser target contained methane. When the gaseous mixture was enriched with methane ([CH_4] > [Ar]) irradiation of the tip of rod target resulted in self-ignition of the flowing gas at the exit from the tube at a distance of 20 cm from the target in the region of contact with atmospheric air. Throughout the whole experiment a spontaneous flame was maintained at the tube exit. Ignition of the laser plume inside the tube resulted in additional coloring of the flame at the tube exit, which became yellow or reddish-orange.

Initially stable at fixed radiation intensity convex shape of the target tip changed with time in the presence of CH_4 - Ar flow by the same manner as by approaching of the target to the focus, i.e. by increasing the intensity. The surface of the target tip became concave and after tens of seconds a conical crater with a diameter of ~1.5 mm and up to several millimeters depth was formed (Fig. 2a). An analysis of the microstructure of the side surface of a laser target showed that interaction of SiO_2 with CH_4 depended on the distance z from the target tip in accordance with the temperature gradient. There were no changes in the surface structure in the zone with a relatively low temperature ($z > 2$ cm) as after annealing in the flame of a methane burner. Uncolored surface husky islands were observed at higher temperatures ($1 < z < 2$ cm). In the zone with a higher temperature ($0.1 < z < 1$ cm) the side surface of a rod became covered by a specular reflecting black film. In the zone with the highest temperature the surface relief at the tip changed more than during irradiation in air. The tip of a target around the region with removed matter was covered by a black glassy film of 50 - 100 μm thickness frothed in the high-temperature zone (Fig. 2b) and smooth in the zone where the temperature was lower at the laser spot periphery. Chip of the film revealed nozzle-like channels of the same characteristic size oriented normally to the surface. The smooth region had fine-grained structure.

The frothed film was displaced on the surface of a glass which was completely covered from the inner side by transparent bubbles of 10 - 20 μm in diameter (Fig. 2c). On the surface of a target irradiated in the high-temperature zone there were hollow spheres with a diameter up to ~100 μm. The spheres were either transparent or outside coated by a white deposited 'soot' and were easily detached (Figs 2d and 2e). Fig. 2f shows bubbles located on the target surface with characteristic traces of a blowout caused by the escape of internal gases. In the low-temperature zone of the glass at a depth up to ~200 μm there were also layers saturated with bubbles with typical size of ~25 μm. Such regions inside some samples contained also whity-brown formations. After irradiation the bottom of a crater remained transparent, i.e. the products of pyrolysis of SiO_2 were removed from the bottom. Instability of the laser target surface resulting on dependence of the rate of etching of SiO_2 at its boundary on the laser radiation intensity was accompanied by shortening of a plume, its subsequent decay, and a reduction of the rate of target 'combustion'.

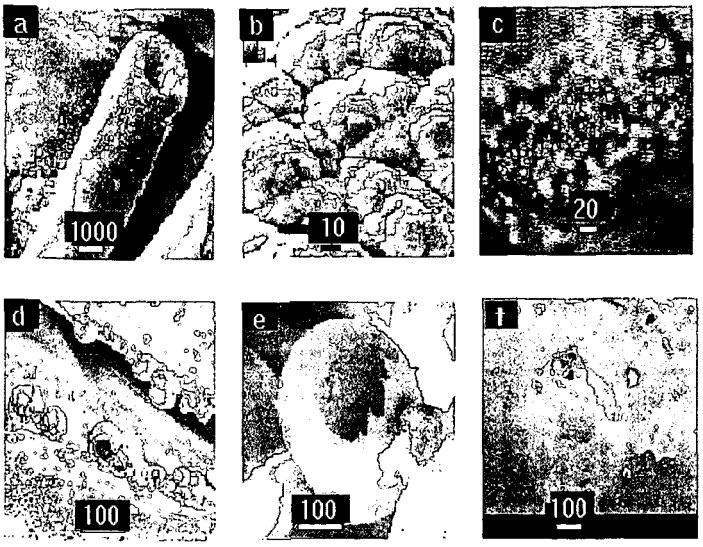

Figure 2. Electron micrographs of laser target (a), boiled and frothed tip of the target (b), bubbles inside (c - photograph) and on surfaces of the targets (d-f).

Vertical convective jet of white smoke emerged from a silica target when the radiation intensity was below the threshold of appearance of a laser plume in an air, $T < T_b$. If the flow of the gas containing CH_4 was repeatedly switched on and off at a constant radiation intensity, a colored plume up to 5 mm length appeared and disappeared in a direction normal to the target tip. This observation indicated that gas-phase reactions took place between the interacting products of a pyrolysis of SiO_2 and CH_4 . Pyrolysis of CH_4 in flowing gaseous mixture interacted with a heated silica rod was indicated by the ejection from the tube of black soot flakes of size up to ~1 cm in accordance with the reaction $CH_4 \rightarrow C + H_2$ at a temperature higher of 800 K. The flakes were formed by a network of filaments of ~0.1 mm in diameter and a very thin layer of a veil-like net between them. These soot flakes emitted bright radiation inside the tube when they crossed the laser beam. It was difficult to carry out x-ray microanalysis because the electron beam destroyed the filaments. There was no self-ignition of the gas by the laser plume when the partial pressure was in the range $1 > [CH_4]/[Ar] > 1/32$ but a self-supporting flame at the tube exit was ignited externally independently on switching the laser plume both on and off. The number of the soot flakes decreased with reducing of CH_4 concentration until they disappeared completely.

Deposition of carried by the flowing gas condensed products on the internal wall of the tube usually lasted the same time as the duration of irradiation of the target (~1 min). The deposited layers were cooled and isolated from the atmosphere by continuing the gas flow for ~30 s after the irradiation. The elemental composition of the deposited materials depended on the partial pressure of methane in the gas flow and deposition place. In particular, the strongly heated surface of the target itself around the laser spot appeared to be a substrate.

A glass-like black film deposited on the target had the chemical composition of a ternary carbosilicate system with depended on temperature concentrations of the components. There were measured ratios of components [Si] : [O] : [C] = 19 : 38 : 42 and 25 : 59 : 16 in two points on the external surface adjoining the tip. On a smooth area of the tip surface around the laser spot ratios [Si] : [O] : [C] = 18 : 21: 60 and 20 : 28 : 52 changed in the direction of a reduction of oxygen and an increase of carbon. This dependence of the composition on the coordinates and, consequently, on the target temperature indicated the reduction reactions occurred on the target.

Black and black-gray layers, mixtures of black and white soot with submicron range microstructure, were deposited on the tube wall when $[CH_4]/[Ar] > 1/16$. The layer thickness reached ~1 mm and the layer density depended on the actual structure of the flowing gas jets determined by the direction of a plume varied during burning of the target and by the local temperature. When the ratio of concentrations in the similar gas flow around a silica target was $[CH]/[Ar] < 1/16$ the ejection of matter from the laser target and the rate of deposition decreased

considerably. The color of the coatings on the tube wall changed being at a distance of 0 - 3 cm from the target tip whity-brown and yellow and at 3 - 15 cm gray. The elemental composition determined at seven points of a pellet compacted from a yellow-brown layer varied within the range [Si] : [O] : [C] = (33:1 - 36:8) : (46:6 - 55:6) : (9:6 - 18.3). The chemical composition of this layer differed considerably from the stoichiometry of the original silica and was the result of the reduction reactions.

DISCUSSION

The chemical composition of final and intermediate products of induced by laser plume chemical reactions was governed by the chemogasdynamic processes on the laser target and between the gas jets containing the products of pyrolysis of methane and silica. Throughout the investigated range of the concentrations $[CH_4]/[Ar]$ used in experiments flammable gases presented in the flow and chemically reducing conditions were maintained. The observed shape of the laser target surface was qualitatively different from that one in oxidizing or neutral ambient gas. It was attributed by narrowing of the thermal energy flux entering target because of additional heating caused by exothermic surface reactions at the maximum intensity in the laser spot. Laser induced chemical reactions occurred not only in gas phase and on the surface but also in the interior of a target, as indicated by laser-induced surface boiling. The appearance of bubbles inside softened silica was attributed by internal gassing occurred when a target was placed in methane flow. Such gas evolution did not occur when plume combustion was maintained in air and Ar. In a control experiment we introduced inside a silica tube of ~2 mm in diameter a bundle of carbon fibers of 10 μm in diameter. Irradiation of the target smelted the fibers with the glass. The glass-fiber boundary was saturated with bubbles and in some cases surrounded by a whity-brown strips.

Boiling of a pure liquid is known to occur because of the appearance of vapor-formation centers, from which bubbles arise inside the liquid, or in a state overheated above the boiling point [9]. The bubbles arise in a liquid if internal pressure $p_i \geq p_a + 2\sigma/r$, where p_a is the atmospheric pressure, σ is the surface tension of silica, r is the bubble radius. In the case under discussion, the quantities σ and r represent the values at the vitrification temperature T_g of silica glass at which the bubble shape becomes frozen. Formation of bubbles from dissolved gases or violent volumetric boiling because of overheating of the liquid phase was not observed in laser targets made of pure silica glass irradiated in atmosphere. Consequently, on the targets streamlined by CH_4 the gas inside the growing bubbles could not consist of the products of pyrolysis of SiO_2 solely becausc p_i could exceed p_a only at temperatures $T > T_b$. The bubbles appeared at lower temperatures and the boundary of the bubble ensemble was mobile at temperatures $T_g \leq T < T_b$.

The most probable reason of observed phenomenon was gas evolution during exothermic chemical reactions in which silica is reduced by carbon and hydrogen occurred inside softened at high temperatures glass. Carbon and hydrogen were appeared on the surface of the rod by pyrolysis of methane and penetrated in the glass by viscous mixing of the melt and diffusion, as indicated by the characteristic shape of whity-brown strips in molten and solidified glass near carbon fibers. Reduction of SiO_2 by carbon $SiO_2 + C \rightarrow Si + SiO + CO$ is used in electrometallurgy for the synthesis of the Si [10]. Silica may be also reduced in the reaction $SiO_2 + H_2 \rightarrow Si + SiO + OH + H_2O$. At temperatures $\sim T_b$ all products of reactions are gaseous because they have lower boiling points. The reactions may cause additional heating of the internal microvolumes of the glass to $T > T_b$ and appearance and growing of microcavities from the gas-formation nuclei filled with gaseous products of the reactions at $p_i > p_a$. A typical shape of the surface at the points of blowout of the bubbles confirmed this hypothesis (Fig.2d). During cooling of the glass the size of the bubbles should decrease and to be frozen at the temperature T_g . This was confirmed by the appearance on a cooled targets of bubbles with concavc dents.

The reduction reactions on the surface of a laser target were initiated at temperatures above the temperature of pyrolysis of methane, ~1 kK, and the rate of these reactions increased with increase in temperature up to the boiling point of silica T_b ~3 kK when a continuous laser plume was formed. The exothermic nature of the reactions was confirmed by lowering of the threshold of formation of a laser plume, when the gas flow contained methane, and supported by increasing of target 'combustion' rate at the maximum intensity in the laser spot as well as by the formation of a crater. The reduction reactions were confirmed also by elemental composition of the laser target surfaces and of the layers of deposited highly disperse products of reactions of whity-brown color. Ratio [Si] : [O] = (79.5 - 46) : (20.5 - 54) on the internal surfaces of four split bubbles indicated that the sample became enriched with silicon being higher of its proportion in silicon monoxide SiO. The reduction processes were observed in experiments with carbon fibers so as droplets of deep-brown color inside the bubbles and evidently formed from more refractory Si and/or SiO.

Deposition of particles on the internal wall of a tube from a high-temperature heterogeneous gas flow occurred under the action of thermophoresys forces similar to the MCVD method employed in the fabrication of silica fiber preforms. Droplets observed inside the bubbles, strips on the boundary of carbon fibers and deposited on substrates powder layers all of yellow, whity- and deep-brown colors are the products of the disproportion reaction of reduced but unstable condensed silicon oxide $SiO \rightarrow Si + SiO_2$. It was last time determined that gradation of color is connected with microstructure of the samples containing amorphous and microcrystalline silicon.

CONCLUSION

Experimentally were established the experimental conditions, the configuration, and the energy and gasdynamic parameters of initiation by cw laser radiation at the 10.6 mm wavelength of chemical reduction of silica streamlined by gas flow containing methane. The exothermic nature of the reduction reactions was confirmed by decrease of the threshold of appearance of a laser plume and increase in the rate of combustion of the target in the laser spot and formation of a crater so as by an increase in the yield of the reaction products deposited on the tube wall, compared with the yield of the products of pyrolysis of silica in air, and also by a fall of the yield when the concentration of methane in the flowing gas was lowered.
The determined final products of laser-induced reactions of silica with methane are conductive carbosilicate films on silica surfaces and reduced silicon oxides in gas and condensed phases.

REFERENCES

1. Dianov E M, Koryakovsky A S, Lebedev V F, Marchenko V M, Prokhorov A M Zh. Tekh. Fiz. 61 (5) 90 (1991) [Sov. Phys. Tech. Phys. 36 551 (1991)]; Sov. Lightwave Commun. 1 223 (1991)
2. Shick H. L. Chem. Rev. 60 331 (1960)
3. Kulikov I. S. Termicheskaya Dissotsiatsiya Soedinenij (Thermal Dissociation of Compounds) (Moscow: Metallurgiya, 1969)
4. Dianov E. M., Lavrishchev S. V., Marchenko V. M., Mashinsky V. M., Prokhorov A. M. Kvantovaya Elektron. (Moscow) 23 1105 (1996) [Quantum Electron. 26 1075 (1996)]
5. Dianov E.M., Koryakovsky A. S., Marchenko V. M., Lebedev V. F., Pimenov V. G., Prokhorov A M Zh. Tekh. Fiz. 63 (11) 196 (1993) [Tech. Phys. 38 1030 (1993)]
6. Sosman R. B. Phases of Silica (New Brunswick, NJ: Rutgers University Press, 1965)
7. Wolf S., Tauber R. N. Silicon Processing for the VLSI Era (Sunset Beach, CA: Lattice Press, 1996)
8. Lavrishchev S.V., Marchenko V.M., Murin D.I. Quantum Electronics, 28, 920 (1998)
9. Kikoin A. K., Kikoin I. K. Molekulyarnaya Fizika (Molecular Physics) (Moscow: Nauka, 1978)
10. Gel'd P. V., Esin O. A. Protsessy Vysokotemperaturnogo Sinteza (Processes in High-Temperature Synthesis) (Sverdlovsk: State Scientific-Research Institute on Ferrous and Nonferrous Metallurgy, 1957)